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Isobaric and isochoric Gruneisen parameters of cubic crystals

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Two new Gruneisen parameters defined by $\gamma_p = -\frac{V}{\nu}\left(\frac{\partial \nu}{\partial V}\right)_p$ and $\gamma_v = -\frac{1}{\alpha \nu}\left(\frac{\partial \nu}{\partial T}\right)_v$ respectively have been calculated for cubic metals, by using Krebs lattice dynamical model which includes the effect of dispersion and crystal anharmonicity. A comparison of the isochoric and the isothermal Gruneisen parameters shows that the isochoric self-energy anharmonic effect which is due to phonon-phonon interaction, is significantly large in the case of alkali metals

1. Introduction

The temperature dependence of the phonon frequencies of a solid is due to isothermal and isochoric anharmonic effects An analysis of the experimental results of Lowndes (1970) in the low temperature range on KBr showed that the phonon frequency shifts due to isochoric self-energy effect is much larger than the isothermal shift which is contrary to the perturbation calculations of Cowley (1963) Therefore we introduced a thermodynamic method (Tolpadi 1975) in which it was shown that the frequency shifts are in satisfactory agreement with the results of Lowndes (1970). In this method we calculated the isochoric Gruneisen parameter by considering the temperature variation of the Debye frequency It was further assumed that the isobaric and the isothermal Gruneisen parameter are the same for all the points of the Brillouin zone. In the present investigation a lattice dynamical method is used to calculate an average isobaric and an isochoric Gruneisen parameter, by considering the temperature variation of the elastic constants in the frequency determinant. As an application of the present theory we have calculated the isobaric and isochoric Gruneisen parameters in the case of eleven cubic crystals.

2. Theory

As discussed earlier, we assume that the phonon frequency shift $\Delta\nu$ is a function of both volume and temperature of the crystal. Therefore when the temperature T and volume V of the crystal change under normal atmospheric pressure P, within the limits of a quasiharmonic model we can write

$$-\Delta\nu = \left(\frac{\partial \nu}{\partial T}\right)_V \Delta T + \left(\frac{\partial \nu}{\partial V}\right)_T \Delta V \qquad (1)$$

where $\left(\frac{\partial \nu}{\partial \bar{T}}\right)_V$ depends on phonon-phonon interaction (Maradudin & Fein 1962) and will be called as self-energy term. The term $\left(\frac{\partial \nu}{\partial \nu}\right)_T$ includes the effect of the change in the interatomic force constant due to the expansion of the lattice

The isochoric Gruneisen parameter γ_V and the isothermal parameter γ_T are defined by,

$$\gamma_V = -\frac{1}{\alpha\nu}\left(\frac{\partial \nu}{\partial \bar{T}}\right)_V, \quad \gamma_T = -\frac{V}{\nu}\left(\frac{\partial \nu}{\partial \bar{V}}\right)_T \qquad \ldots (2)$$

where α is the volume expansion coefficient

Introducing the value of γ_V and γ_T in eq. (1) we can show that the isobaric Gruneisen parameter γ_P is given by,

$$\gamma_P = -\frac{V}{\nu}\left(\frac{\partial \nu}{\partial \bar{V}}\right)_P = -\frac{1}{\nu}\left(\frac{\partial \nu}{\partial \bar{T}}\right)_P = \gamma_V + \gamma_T. \qquad \ldots (3)$$

The isobaric Gruneisen parameter is calculated directly as follows Krebs (1965) model is used to calculate the temperature variation of the phonon frequencies of the crystal along the symmetry directions (100),(110) and (111) respectively The appropriate isothermal elastic constant and thermal expansion data are considered in solving the frequency determinant The isobaric phonon Gruneisen parameter $\gamma_P = -\frac{1}{\alpha\nu}\left(\frac{\partial \nu}{\partial \bar{T}}\right)_P$, for a given mode of vibration along the symmetry direction is calculated from a knowledge of the temperature variation of the phonon frequencies. It may be noted that for a given point in the Brillouin zone there is one longitudinal and two transverse modes of vibration The isobaric phonon Gruneisen parameters for the two states of polarisation are calculated along the symmetry directions of the crystal by taking into account the temperature vibration of the phonon frequencies Therefore an average phonon Gruneisen parameter for the relevent direction at any given temperature can be calculated. Now the average isobaric Gruneisen parameter for the crystal is obtained by using Houston's formula (Houston 1948, Betts *et al* 1956) which is given by

$$\bar{\gamma}_P = (10\bar{\gamma}_A + 16\bar{\gamma}_B + 9\bar{\gamma}_C)/35, \qquad \ldots (4)$$

where $\bar{\gamma}_A$, $\bar{\gamma}_B$ and $\bar{\gamma}_C$ are the average isobaric phonon Gruneisen parameters along the symmetry directions (100), (110) and (111) respectively, by considering the transverse and longitudinal polarisations

Table 1 Isobaric, isothermal and isochoric Gruneisen parameters of cubic crystals

Crystal	Temperature in °K	Gruneisen parameters			
		$\bar{\gamma}_P$ (Isobaric)	γ_T (Isothermal)	$\bar{\gamma}_V$ (Isochoric)	$\frac{\bar{\gamma}_V}{\gamma_T}$
Ag	275	3 3	2 40	0 9	4
Cu	280	3 1	1 97	1 1	56
Pb	280	4 7	2 73	2 0	.71
Al	280	4 0	2 10	1 9	90
Ni	280	3 6	1 88	1 7	91
Fe	280	2 1	1 6	5	0.3
W	280	2 7	1 62	1.0	0 6
Mo	280	3 3	1 57	1 7	1 1
Na	165	2 8	1 25	1 6	1 3
Rb	110	3 2	1 25	2 0	1 6
K	178	3.5	1 18	2 3	1.9

3 Results

In the present study the average isobaric Gruneisen parameters have been been calculated in the case of cubic metals in the room temperature range But in the case of alkali metals temperature variation of the elastic constant data is not available in the room temperature region and therefore the isobaric Gruneisen parameter has been calculated in the neighbourhood of 150°K The temperature variation of the isothermal elastic constant data has been calculated by using the compilation made by Simmons & Wang (1971). Using the elastic constant, thermal expansion (Hindert & Krider 1957) and other relevent data the average isobaric Gruneisen parameter is calculated from eq. (4) by adopting Krebs (1965) model. Appropriate form of the frequency determinant is used when considering the crystals belonging to fcc and bcc structures The face centered cubic metals investigated are silver, copper aluminium, nickel and lead and the body centered cubic crystals are iron, tungsten, molybdenum, sodium, rubidium and potassium The calcuated isobaric Gruneisen parameters are given in table 1 The isothermal Gruneisen parameters (Gruneisen 1926) calculated at the corresponding temperature for these crystals are also given in table 1. Now using eq. (3) an average isochoric Gruneisen parameter $\bar{\gamma}_V = \bar{\gamma}_P - \gamma_T$ is obtained. A comparison of γ_T and $\bar{\gamma}_V$ shows that isochoric self-energy effect is significant in all cases and it is particularly large in the case of alkali metals.

The main purpose of the present investigation is to introduce a lattice dynamical method to calculate two new Gruneisen parameters $\bar{\gamma}_P$ and $\bar{\gamma}_V$. A comparison of these new parameters gives an idea of the contribution to crystal anharmonicity due to isothermal volume expansion and isochoric selfenergy effect which is due to phonon-phonon interaction

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